# THE IMPACT OF MICROBIOLOGICALLY INFLUENCED CORROSION

ON PROTECTIVE POLYMER COATINGS

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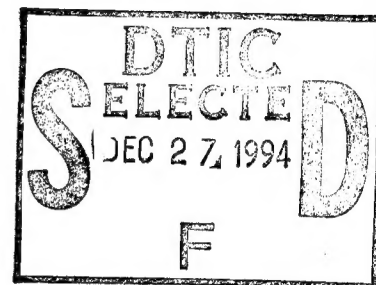
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ABSTRACT

Thirteen polymer coating systems on steel have been exposed to Pacific ocean water (NS) and artificial seawater (AS). Impedance data and electrochemical noise data have been obtained for two-electrode systems on a weekly basis. For comparison three-electrode impedance measurements have been performed on a monthly basis. Noise data were obtained several times each week. The impedance and noise data at the Port Hueneme, CA test site (NS) were collected by an on-site computer system with a multiplexer which is controlled via modem by a computer system at CEEL/USC. In the laboratory a more traditional approach was used. Experimental data for two coating systems exposed to NS and AS for three months showed that the experimental approach developed for data collection at a remote test site produced reliable results which were in general agreement with results obtained in the laboratory.

Keywords: polymer coatings, steel, seawater, electrochemical impedance spectroscopy, electrochemical noise analysis, corrosion monitoring

A-1

INTRODUCTION

The impact of microorganisms on corrosion protection by polymer coatings is being evaluated at present for different coating systems on steel during exposure to natural Pacific seawater at Port Hueneme, California. Subsequent tests are planned for exposure at Fort Lauderdale, Florida. Coating performance is evaluated by analysis of impedance spectra and electrochemical noise data. Electrochemical impedance spectroscopy (EIS) has been shown to be a powerful non-destructive tool for the evaluation of coating properties and their changes with exposure time [1-4]. The application of electrochemical noise analysis [ENA] is relatively new. Results obtained in laboratory tests for two of the coatings systems to be studied in the present project have been discussed elsewhere [5,6].

Since impedance and noise measurements have to be performed for a large number of samples at a remote test site, it was necessary to develop a new approach for monitoring coating properties. A multiplexer was used to collect data for 13 coatings systems. The experiments were performed by an on-site computer which was controlled via modem by a computer system at CEEL/USC using software developed for this purpose. Since simultaneous collection of potential and current noise data requires a two-electrode system [5-7], impedance data were collected for the same system. Impedance spectra were also obtained once a month for each of the two samples using a three-electrode system. Generally, noise data were obtained several times per week for all 13 coatings, while impedance data were collected once a week. In order to illustrate the experimental approach developed for remote monitoring of coating performance using EIS and ENA, data obtained for two coating systems with different performance will be presented. A more detailed analysis of the EIS and ENA data for exposure to natural (NS) and artificial (AS) seawater will be presented elsewhere [8]. The impact of different colonies of bacteria on coating performance is being studied at present in laboratory experiments [9]. After different exposure periods the coating properties will be evaluated by EIS. Exposed samples will also be analyzed with an environmental scanning electron microscope (ESEM) to determine biofilm distribution and spatial relationships between coating damage and microorganisms [9].

EXPERIMENTAL APPROACH

Materials and Methods

Materials

Twelve different coating systems (Table I) were selected for this study. Samples of the CR series were obtained from the Steel Structures Painting Council (SSPC), Pittsburgh, PA, while samples of the JJ series were coated by AAA Plating, Compton, CA. CR-9 and JJ-7 had the same coating formulation. Care was taken to protect the edges and corners of the coated samples. This was achieved by applying a thicker layer of paint for the samples of the CR series and by applying a thin layer of paint after coating application for the JJ series. Each coupon of the dimensions 152 cm x 102 cm (6" x 4") had an exposed area of about 250 cm^2. Table I also contains the coating thickness of the samples exposed to seawater. Average thickness values for the CR series are given for both sides of each of the two samples used for collection of EIS and ENA data, while average values for the JJ series were obtained as part of quality control at AAA Plating. There is a significant difference in coating thickness for CR-9 and JJ-7 prepared according to the same specifications.

In preliminary experiments one sample of each coating system was exposed to AS for 24 h before measurement of an impedance spectrum on a 20 cm^2 area. All samples for the CR series showed only one time constant suggesting intact coatings. However, coatings JJ 1 - 6 showed two time constants which could be indications of pre-existing conducting paths [1-4].

Exposure Conditions

All 13 coating systems were exposed to Pacific Ocean seawater at Port Hueneme, CA and to synthetic sea water (Instant Ocean) at CEEL/USC. At Port Hueneme samples were suspended into a plastic tank through which natural seawater was flowing at a rate of 0.5 l/min. A Ag/AgCl reference electrode was placed between each of the two samples used to collect EIS and ENA data. A Faradaic cage was placed around the water tank. A block diagram of the experimental arrangement is given in Fig. 1. The same arrangement was used in the laboratory experiments except that stagnant conditions were used. A problem with the collection of electrochemical data was detected in the preliminary stages of the project at Port Hueneme. A large off-set current affecting the measurements was particularly bothersome for the noise measurements. This grounding problem was solved to a large extent by setting up a system in which seawater was dripping in and out of the tank rather than flowing in and out of the tank.

Methods

Impedance and electrochemical noise data were measured using a two-electrode arrangement as described previously for the simultaneous collection of noise data [5-7]. The necessity of collecting data by remote control led to development of a new approach for monitoring of the properties of polymer coatings during exposure to seawater. This approach will be described briefly in the following.

Each sample pair occupied one input channel of a multiplexer (Fig. 1) which is a 2 x 20 switch unit. Each input channel has two electrically isolated leads which were switched together either into connection or disconnection with the two leads of the main output. Whenever a channel was switched in, the two leads of the multiplexer main output were connected with the two samples of the pair occupying that channel. The isolation resistance between the two leads of a channel and between channels are greater than 10^{10} Ω.

The voltmeter and the potentiostat formed the electrochemical noise measurement unit. The general approach for simultaneous collection of potential and current noise was the same as discussed previously [5-7]. When a pair of coated samples was switched into connection with the noise measurement unit, the potentiostat applied 0 mV potential difference between the two samples. The current fluctuations between the pair were measured by the potentiostat. One lead of the voltmeter was switched into connection with one of the samples, while the other lead of the voltmeter was connected to the Ag/AgCl reference electrode. Since the potential difference between the two samples was 0 mV, the voltmeter was measuring the potential fluctuations of the couple vs. the reference electrode. A modified version of the previously developed noise data acquisition software [5-7] was used to control the voltmeter and the potentiostat for simultaneous sampling of potential and current fluctuations at a rate of 2 points/sec.

For impedance measurements an approach which differs from the traditional scheme had to be used. The poor high frequency (>100 Hz) current response of the multiplexer caused distortion of the ac signals when the impedance measurements using a potentiostat were performed. Therefore the frequency response analyzer (FRA) with a signal generator and two analyzers was applied for impedance measurements. When a coated sample pair was switched into connection with the FRA, an accurate resistor was placed in series with the sample pair. The voltage signal generated by the FRA was applied across the coupon pair and the resistor. The response to the signal applied across the sample pair was determined by one analyzer and compared with the total voltage signal measured by the other analyzers. Since the value of the resistor is known, the impedance of the coated sample pair can be calculated. For decreasing frequencies

4

the initial resistor was replaced automatically by a series of others resistors with higher values. A newly developed impedance data acquisition program was used for collecting the data and controlling the FRA.

All measurement operations are fully controlled by computer programming, including input channel switching, instruments synchronization, noise and impedance data collection. In one measurement, only one input channel can be allowed to switch into connection with main output. In noise measurements, only the voltmeter and the potentiostat can be connected with the multiplexer main output, while during impedance measurements, the main output is only in connection with the FRA without connection to the noise unit. In this way, only one pair of coated samples is measured once for either noise or impedance at any given time.

A modem was installed inside the on-site computer at the Port Hueneme test site, which controlled the measurement and allowed corrosion monitoring by remote control. Both the on-site computer and a remote-site computer were installed with compatible modems and corresponding communication software for computer communicating through a telephone line. Software and hardware arrangements allowed the remote-site computer connection through the telephone line with the on-site computer resulting in the remote-site computer taking control over the on-site computer. Therefore the measurement could be set up at the remote site and data collected at this site could be transferred to the remote site.

In the laboratory tests the instrumentation was basically the same as at the Port Hueneme test site except that the multiplexer and modem were not used.

EXPERIMENTAL RESULTS AND DISCUSSION

The results obtained during three months exposure for two coating systems - CR-6 and CR-9 (Table I) - will be used to illustrate the type of results collected by remote control at the test site in Port Hueneme with EIS and ENA. These results will be compared with those determined with a more traditional approach in laboratory tests. CR-6 consists of a zinc-rich primer followed by a epoxy polyamide and a latex coating (Table I). CR-9 is an all-epoxy polyamide coatings system. Previously no significant degradation of the coating properties had been observed for CR-9 during exposure to 0.5 N NaCl for one year [2,3,10]. The performance of CR-6 in the same tests was also satisfactory and better than that of CR-1, CR-2 and CR-5. The results obtained in the present tests for the other coating systems in Table I will be discussed elsewhere [8].

5

The impedance spectra for CR-9 remained capacitive during the entire test period, while two time constants could be resolved already after one week exposure for CR-6 indicating that some conducting path probably due to defects in the coating were present. This observation is different from previous results [2,3,10]. Fig. 2 shows impedance spectra recorded for CR-6 after about two months exposure to NS and AS. The spectra are in general agreement with the model for the impedance of polymer coatings on metals [1-4,10]. The spectra in Fig. 2 were recorded with the two-electrode arrangement used for collection of EIS and ENA data (Fig. 1). Fig. 3 shows spectra obtained for CR-6 with a three-electrode arrangement for each of the two coated samples in Fig. 2. The spectra obtained in NS show very similar behavior for both samples (Fig. 3a), while sample #1 in AS has lower values of the pore resistance R_{po} than sample #2 (Fig. 3b) comparable to the two samples in NS. In comparing results in Fig. 2 and 3 it will be noted that the spectra obtained for the 2-electrode system are close to the average of the spectra obtained for the individual samples. Although the impedance spectra indicate some loss of protection for CR-6, R_{po} had very high values of about 10^7 ohm.cm^2. Visual inspection after 30 days of CR-6 exposed in the laboratory revealed one small rust spot on one sample and two on the other. After 90 days 2 and 3 spots, respectively, were observed.

The spectra for CR-9 remained capacitive over the three-month test period (Fig. 4). The impedance exceeded 10^{10} ohm.cm^2 at the lowest frequencies indicative of a very protective coating. Due to this very high impedance values the scatter of the experimental data became quite high especially in Port Hueneme where the potentiostat was replaced by two resistors and a multiplexer was used to collect data from the 13 coating systems.

The time dependence of the coating capacitance C_c is shown in Fig. 5 for exposure for CR-6 (Fig. 5a) and CR-9 (Fig. 5b). After an initial increase in both media due to water uptake by the coating, C_c for CR-6 became more or less constant in NS, but continued to increase in AS (Fig. 5a). For CR-9 C_c became constant after about two weeks with similar values in NS and AS.

Fig. 6 gives a comparison of the R_{po} values obtained for CR-6 in NS and AS with the 2-electrode and 3-electrode systems. As mentioned before, the values determined for the 2-electrode system are about the average of the R_{po} data obtained for the 3-electrode system. This result suggests that the much simpler 2-electrode system for collection of electrochemical noise data can provide reliable qualitative results concerning coating degradation. It is interesting that R_{po} did not show the expected decrease with time suggesting that the initial coating defects did not increase

significantly to make a major contribution to the impedance of the relatively large sample (250 cm^2).

The time dependence of the noise resistance $R_n = \sigma[V(t)]/\sigma[I(t)]$ obtained as the ratio of the standard deviation $\sigma[V(t)]$ of the potential fluctuations and $\sigma[I(t)]$ of the current fluctuations [5-7] is given in Fig. 7 for CR-6 (Fig. 7a) and CR-9 (Fig. 7b) for exposure in NS and AS. Similar behavior was observed for CR-9 in both media with higher values of R_n.

Spectral noise plots [5-7] obtained after about two months exposure to NS and AS are shown in Fig. 8 for CR-6 (Fig. 8a) and CR-9 (Fig. 8b). The values of R_{sn} calculated from the experimental potential and current fluctuations for CR-6 did not show a significant frequency dependence in the measured frequency range between 1 Hz and 1 mHz (Fig. 8a). Higher values of R_{sn} and a more pronounced frequency dependence were observed for CR-9 (Fig. 8b).

The time dependence of the spectral noise resistance R^o_{sn} obtained from the data in Fig. 9 as the dc limit, is similar to that observed for R_n in Fig. 7 in both media with higher values of R^o_{sn} for the more protective coating system CR-9 (Fig. 9).

Comparison of the time dependence of R_{po}, R_n and R^o_{sn} for CR-6 shows that similar values were obtained during exposure to NS with less fluctuations for R_{po} (Fig. 10a). In AS a gradual decrease of R_n and R^o_{sn} was observed, while R_{po} remained more or less constant (Fig. 10 b).

CONCLUSIONS

The general agreement of electrochemical impedance and noise data for two coatings systems of different performance via remote control with corresponding data obtained in laboratory experiments using a more traditional approach suggests that the experimental approach developed for monitoring coating performance provides satisfactory results. Since a multiplexer was used to collect impedance and noise data for 13 different coating systems at the remote test site, a potentiostat could not be used to collect impedance data. Nevertheless, R_{po} showed similar values and similar time dependence in field and laboratory tests during the initial stages of exposure.

Comparison of R_{po} and the values of R_n as well as R^o_{sn} shows similar trends. Since collection of noise data is quite simple provided suitable software for simultaneous measurement of potential and current noise is used and since the cost of the equipment is low compared to that for impedance measurements, it appears the ENA can become a valuable tool for monitoring of coating performance at remote locations. More

information concerning the usefulness of ENA will become available when experimental data for the 13 different coating systems exposed to natural and artificial seawater for 6 months are analyzed and compared to EIS and surface analytical data.

ACKNOWLEDGEMENT

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TABLE I(a)
COMPOSITION AND THICKNESS OF COATING SYSTEMS (CR Series)

Sample Name	CR1	CR2	CR5	CR6	CR7	CR9
Substrate	Hot Rolled Steel	Hot Rolled Steel	Hot Rolled Steel	Hot Rolled Steel	Hot Rolled Steel	Hot Rolled Steel
Primer	Alkyd high solid[1]	Alkyd high solid[1]	Zn-rich Primer[4]	Zn-rich Primer[4]	Epoxy Polyamide[5]	Epoxy Polyamide[5]
Midcoat	Low VOC Alkyd[2]	Silicone Alkyd[3]	Epoxy Polyamide[5]	Epoxy Polyamide[5]	Epoxy Polyamide[8]	Epoxy Polyamide[8]
Topcoat	Low VOC Alkyd[2]	Silicone Alkyd[3]	Urethane[6]	Latex[7]	Latex[7]	Epoxy Polyamide[9]
Thickness(μm) sample#1, AS	165/158	141/117	264/236	213/226	186/205	181/191
Thickness(μm) sample#2, AS	193/160	125/118	264/254	216/234	197/205	200/187
Thickness(μm) sample#1, NS	154/168 –	121/131	307/279	274/290	187/204 –	180/196
Thickness(μm) sample#2, NS	144/173	118/127	302/297	287/295	189/191	196/205

1.TT-P-645B ; 2.TT-E-489H ; 3.TT-E-49 ; 4.SSPC-20, type 2 ; 5.MIL-P-24441,Formula 150 ; 6.MIL-C-85285 ; 7.MIL-P-28578 ; 8.MIL-P-24441,Formula 151 ; 9.MIL-P-24441,Formula 152

TABLE I(b)
COMPOSITION AND THICKNESS OF COATING SYSTEMS (JJ Series)

Sample Name	JJ1	JJ2	JJ3	JJ4	JJ5	JJ6	JJ7
Substrate	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel	Cold Rolled Steel
Primer	Zinc plate[a]	Zinc plate[a]	Phosphate coat[d]	Phosphate coat[d]	IVD-Al[e]	IVD-Al[e]	Epoxy Polyamide[5]
Midcoat	Epoxy[b]	Epoxy[b]	Epoxy[b]	Epoxy[b]	Epoxy[b]	Epoxy[b]	Epoxy Polyamide[8]
Topcoat		polyurethane[c]		polyurethane[c]		polyurethane[c]	Epoxy Polyamide[9]
Ave. thickness (μm)	53	83	43	76	81	81	71

a. Zinc plate per QQ-Z-325 Rev. C (Type II, Class 2).
b. 2 coats of epoxy polyamide primer MIL-P-23377 Rev. F (Type I Class 3) per MIL-F-18264 REV.D AMD.1.
c. 1 coat of MIL-C-85285 REV.B (AS) AMD.2 polyurethane per MIL-F-18264 REV.D AMD.1 color #36375 lusterless gray of FED-STD-595 .
d. Phosphate coat DOD-P-16232 REV.F (Type Z Class 3) ; hydrogen embrittlement relieved for 8 hours at 210-225 degree.
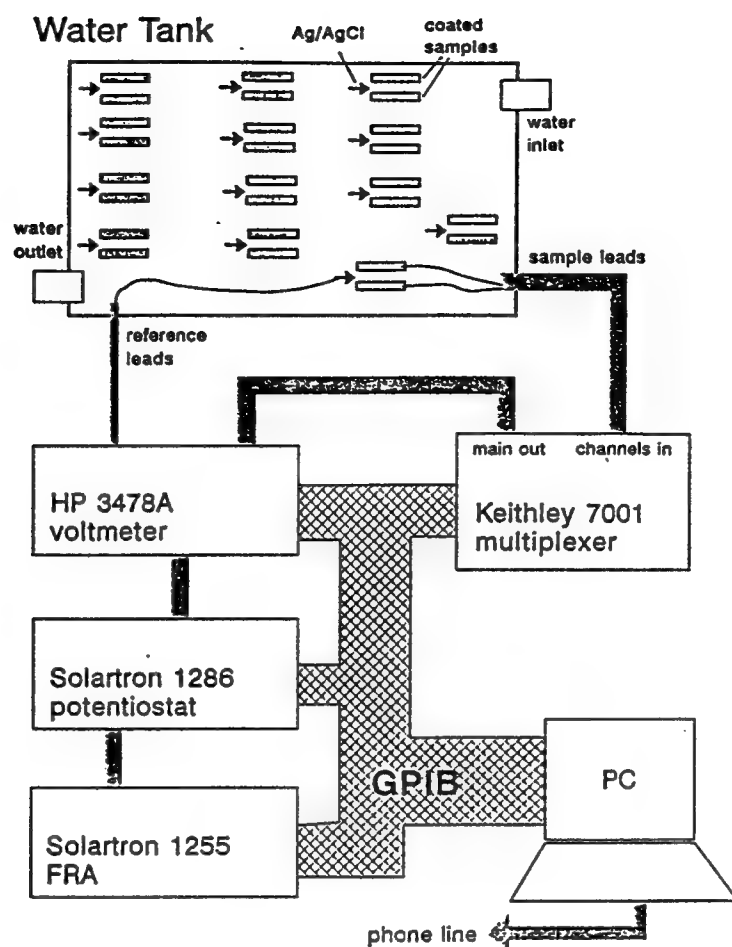e. IVD-aluminum per MIL-C-83488-C (Notice 1, Type II Class 1).

Fig. 1. Block diagram for the experimental arrangement
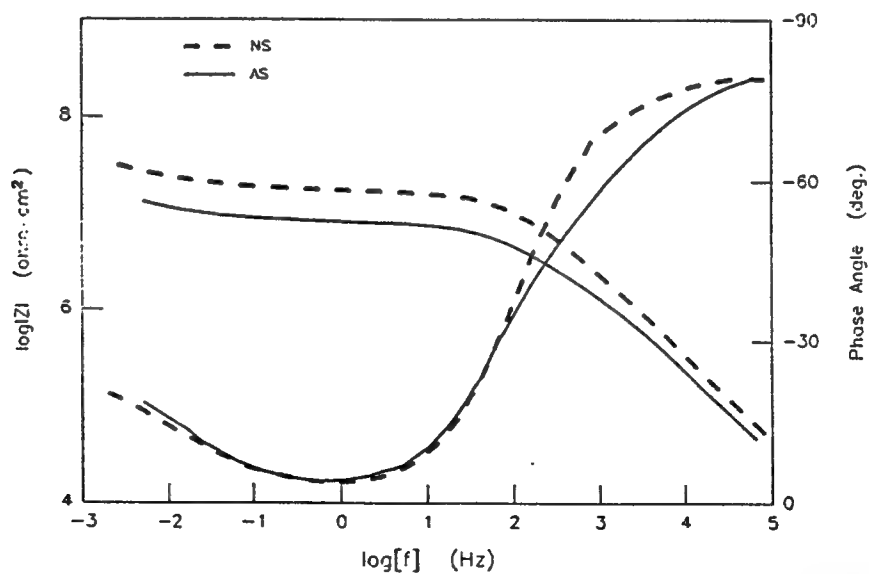at the Port Hueneme test site.

Fig. 2. Bode plots for coating CR-6 recorded after two months exposure
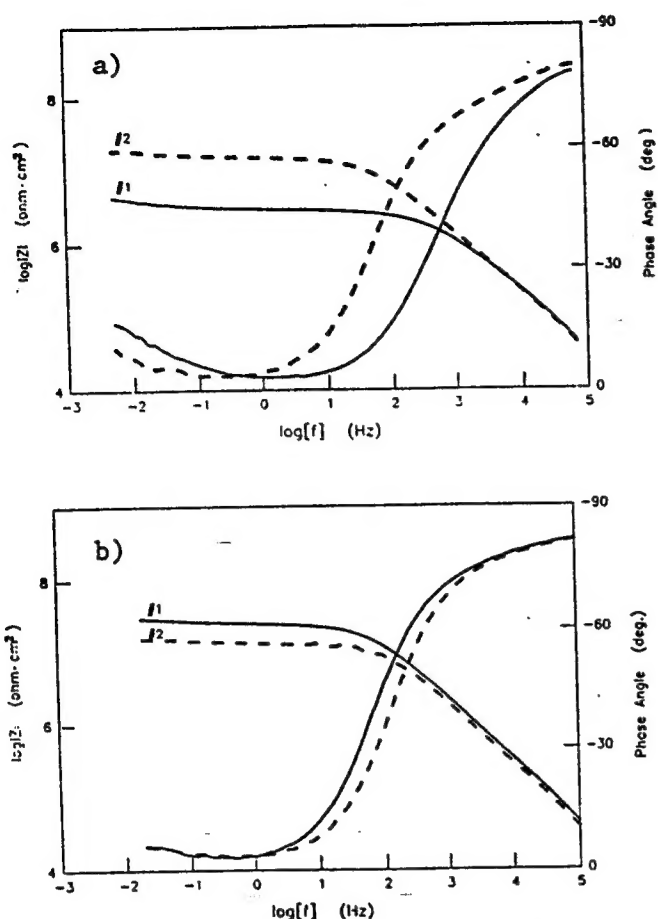to natural seawater (NS) and artificial seawater (AS); two-electrode cell.

Fig. 3. Bode plots for two samples of coating CR-6 exposed for 70 days (#1) or 69 days (#2) to natural seawater (Fig. 3a) and for 76 days (#1) or 77 days (#2) to artificial seawater (Fig. 3b).; three-electrode cell.
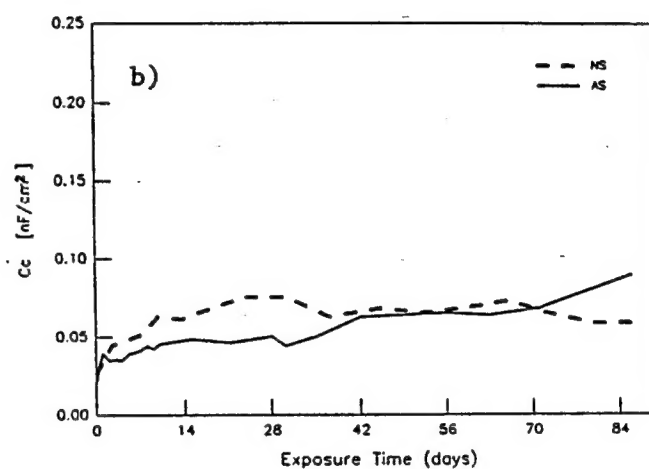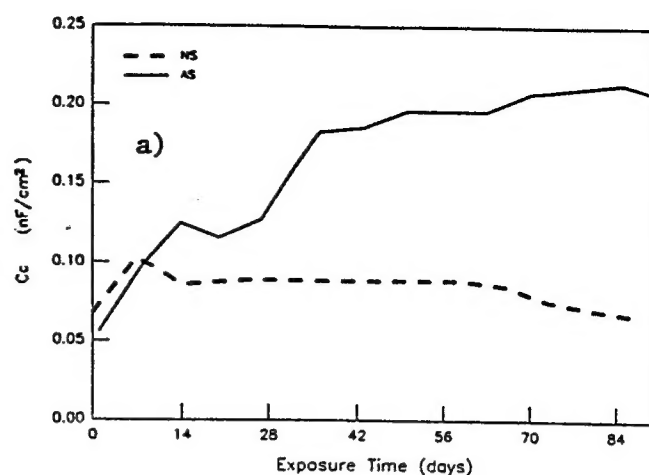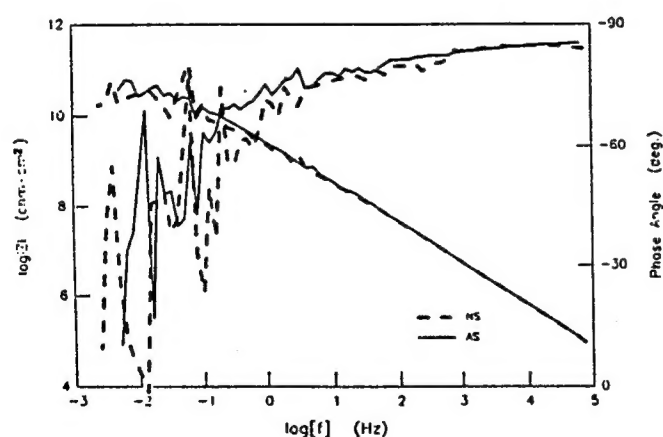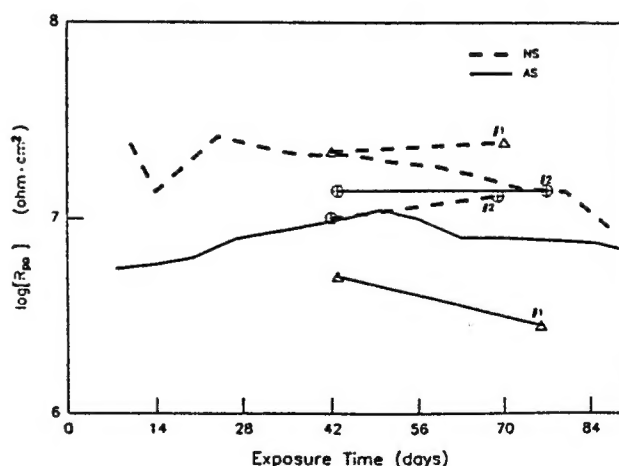

Fig. 5 Time dependence of coating capacitance C_c for CR-6 (Fig. 5a) and CR-9 (Fig. 5b) exposed to natural and artificial seawater.

Fig. 4. Bode plots for coating CR-9 recorded after two months exposure to natural seawater (NS) and artificial seawater (AS); two-electrode cell.

Fig. 6 Time dependence of pore resistance R_{po} for coating CR-6 as a function of exposure time to natural (NS) and artificial (AS) seawater; data for two- and three- electrode cells.
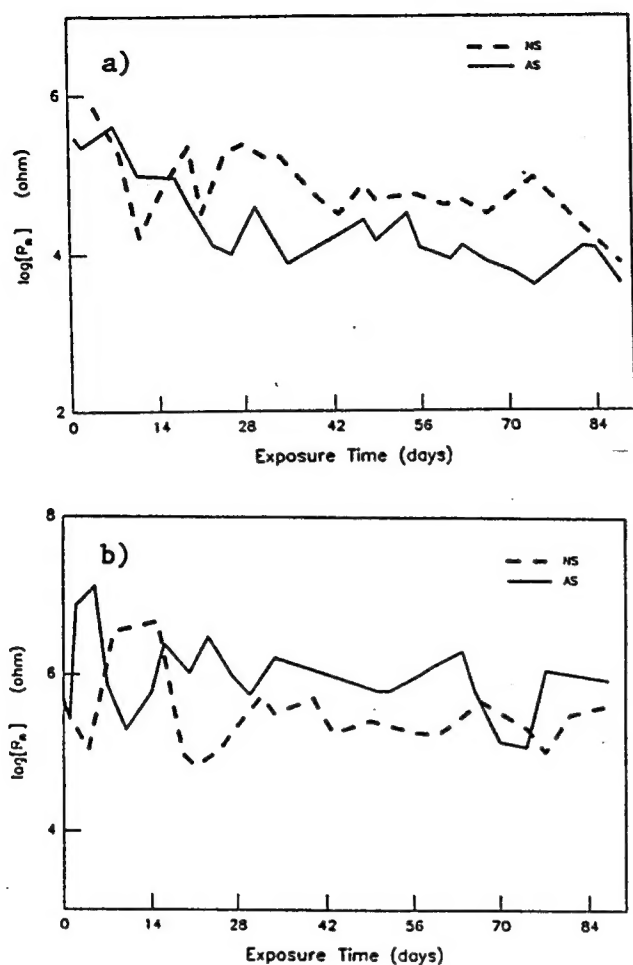
Fig. 7 Time dependence of noise resistance R_n for coatings CR-6 (Fig. 7a) and CR-9 (Fig. 7b) exposed to natural (NS) and artificial (AS) seawater.
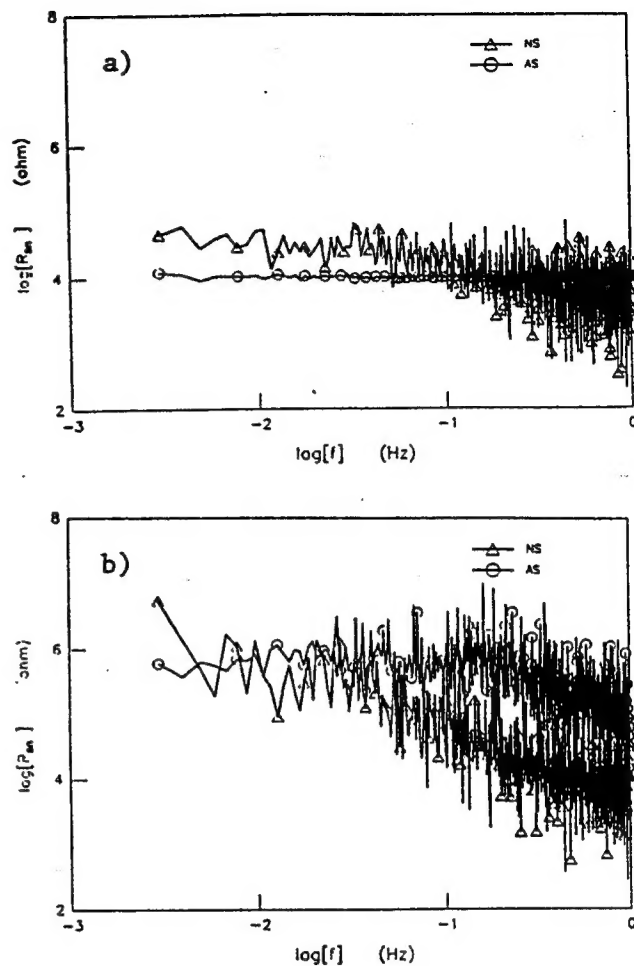
Fig. 8 Spectral noise plots for coatings CR-6 (Fig. 8a) and CR-9 (Fig. 8b) after 63 days exposure to natural (NS) and artificial (AS) seawater.
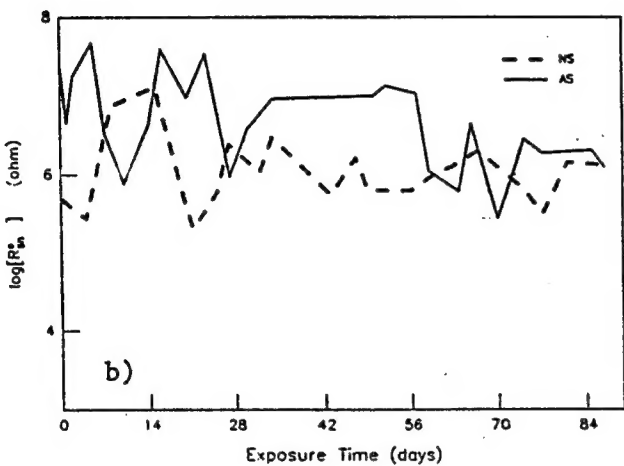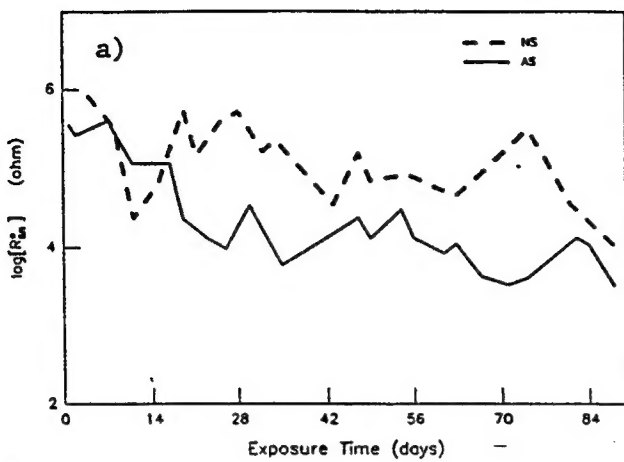
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Fig. 9 Time dependence of spectral noise resistance R^o_{sn} for coatings CR-6 (Fig. 9a) and CR-9 (Fig. 9b) exposed to natural (NS) and artificial (AS) seawater.

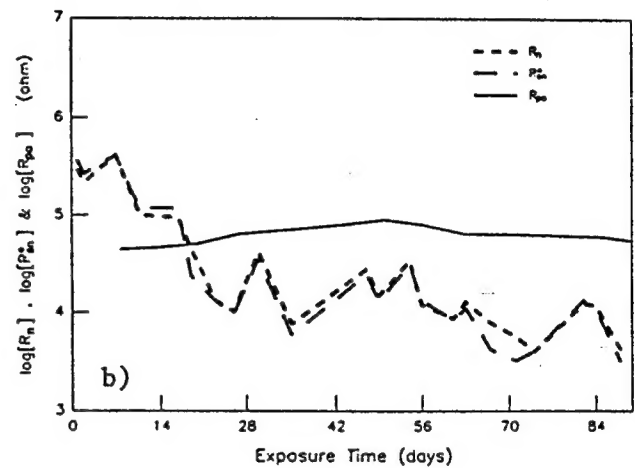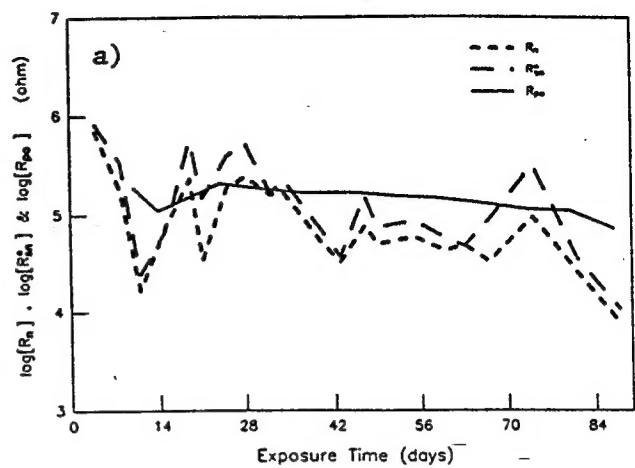Fig. 10 Time dependence of R_{po}, R_n and R^o_{sn} for coating CR-6 as a function of exposure time to natural (Fig. 10a) and artificial seawater (Fig. 10b).

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

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